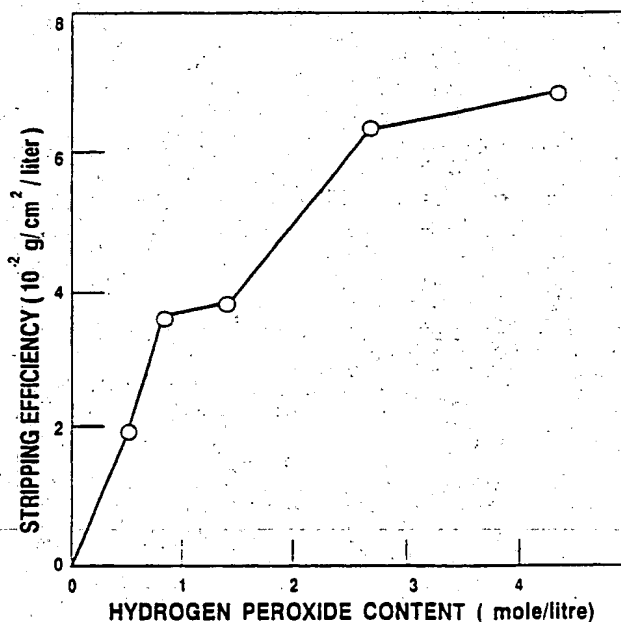


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(54) Title: STRIPPING SOLUTION AND PROCESS FOR STRIPPING COMPOUNDS OF TITANIUM FROM BASE METALS

**(57) Abstract**

An aqueous stripping solution and method for selectively removing a titanium compound from a base metal. The aqueous solution contains a source of hydrogen peroxide, an alkali source of hydroxyl ions and an acid with the components in a concentration such that the pH of the solution is above 8.

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**STRIPPING SOLUTION AND PROCESS FOR STRIPPING
COMPOUNDS OF TITANIUM FROM BASE METALS**

Field of the Invention

This invention is a continuation-in-part of U.S. Patent Application Serial No. 599,833 filed October 19, 1990 and relates to an aqueous stripping solution for selectively removing a titanium compound, such as TiN or TiB₂, from a solid base metal without chemically attacking the solid base metal and to an accompanying process for stripping compounds of titanium from base metals.

Background of Invention

High performance components in aircraft engine turbomachines such as compressor blades, bearings and gears are typically coated with a titanium metal compound such as TiN to improve their wear characteristics and to provide erosion protection. The engine parts are cast or otherwise molded or machined from superalloys, stainless steels or alloy steels and represent very expensive precision components. Removal of the coating from the underlying base metal is necessary if a defect is discovered in the coating and/or for restoring worn components. It is essential to strip the protective coating from the base metal without suffering any detrimental attack to the underlying base metal.

To selectively strip a titanium compound such as TiN from a solid base metal composed of a superalloy, stainless steel or alloy steel without

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chemically attacking the base metal is particularly difficult when both the base metal and coating have a high corrosion resistance characteristic. Stripping is even more difficult when the corrosion resistance of the coating is equal to or greater than the corrosion resistance of the substrate.

Although, stripping solutions containing hydrogen peroxide are known there is no known aqueous based stripping solution using hydrogen peroxide which will permit the removal of a coating of a titanium compound from a solid base metal composed of a superalloy, stainless steel or alloy steel without causing detrimental attack to the underlying base metal. A chemical stripping solution comprising hydrogen peroxide is described in U.S. Patent Nos. 4,554,049, 4,410,396 and 4,545,918 respectively. The stripping solutions disclosed in these patents are either unable to strip compounds of titanium from base metals composed of superalloys stainless steels and alloy steels or will actively attack both the titanium compound coating and the base metal.

Summary of the Invention

The process of the present invention for stripping a coating of a titanium compound from an underlying base metal without suffering chemical attack to the base metal comprises the steps of:

immersing the base metal and coating into an aqueous solution containing a source of hydrogen peroxide, an alkali source of hydroxyl ions, and an

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acid, maintaining the solution temperature between 25°C and 85°C and adjusting the molar ratio of the components to cause the pH of the aqueous solution to be above a pH of 8.

The stripping composition of the present invention comprises an aqueous solution including an alkali source of hydroxyl ions, a source of hydrogen peroxide and an acid with the constituents of the solution in a concentration such that the pH of the solution is above 8.

Brief Description of the Drawings:

Figure 1 is a plot of stripping efficiency versus the content of the preferred acid in mole per liter for removing a TiN coating from an Inconel 718 base metal;

Figure 2 is a plot similar to that of Figure 1 showing stripping efficiency as a function of the content of NH_4OH in mole per liter in the stripping solution of the present invention;

Figure 3 is another plot similar to that of Figure 1 of stripping efficiency as a function of the content of hydrogen peroxide in mole per liter in the stripping solution of the present invention;

Figure 4 is a plot of the solution stripping rate for stripping TiN from an Inconel 718 coupon as a function of the solution operating temperature; and

Figure 5 is a plot of the solution active life of a preferred solution composition for removing TiN from Inconel 718 base metal substrates and the stripping efficiency as a function of temperature.

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Detailed Description of the Invention

Essentially any coating composition of a titanium compound can be removed from any base metal substrate by the process of the present invention without detrimentally attacking the base metal. The invention is particularly suited to the removal of TiN or TiB₂ from a base metal composed of stainless steels, superalloys or alloy steels.

The stripping solution of the present invention comprises the following three components: a source of hydrogen peroxide, an alkaline source of hydroxyl ions and a suitable acid in various proportions to cause the pH of the solution to be above 8 without corroding the substrate. The stripping solution is prepared by first combining the source of hydrogen peroxide with water. The source of hydrogen peroxide should be present in a minimum concentration of .29 mole per liter and in a preferred concentration range of between .29 to about 4.71 mole per liter (mole/L). Any source of hydrogen peroxide such as a perborate, as is well known to those skilled in the art, may be used. Other compounds which readily dissociate into hydrogen peroxide upon contact with water are also suitable. The alkali source of hydroxyl ions (OH) is then added to the solution. The hydroxyl ion is preferably added in combination with ammonium ions through the addition of ammonium hydroxide (NH₄OH). The source of hydroxyl ions should be present in the stripping solution in a concentration of at least 0.29 mole/L

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and preferably between .29 mole/L and 3.23 mole/L. An acid must also be present in the solution at a concentration of 0.026 mole/L and preferably between 0.026 mole/L and 0.76 mole/L. Any acid which will not corrode the base metal may be used, preferably an organic carboxyl or carboxyl-hydroxyl group acid such as lactic acid, oxalic acid, tartaric acid, formic acid, propionic acid or citric acid. Alternatively, a diluted inorganic acid such as, for example, acetic acid, nitric acid, hydrochloric acid and sulfuric acid may also be used provided it will not chemically attack the base metal and is low enough in concentration to maintain the solution pH above 8.

The pH of the stripping solution is critical to the present invention and must be above pH 8 to be effective. The preferred pH range is between pH 9-14 with a pH range of 10-12 being optimum. The pH of the solution may be controlled by adjusting the concentration of alkali, peroxide and organic acid relative to one another provided each is held to a concentration within the preferred range. Additionally, other alkali ions such as sodium or potassium ions may be added to the stripping solution by the addition of NaOH and/or KOH to establish the desired mole concentration and/or to adjust the pH of the solution.

The effectiveness of the stripping solution of the present invention is determined by the efficiency in which the titanium compound coating is removed from the substrate without suffering any deleterious effect on the base metal. A minimum stripping efficiency of $1 \times 10^{-2} \text{g/cm}^2/\text{L}$ and

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preferably above $2 \times 10^{-2} \text{g/cm}^2/\text{L}$ is necessary for the stripping solution to be acceptable for commercial practice. The stripping efficiency is determined based on total weight loss of the coating per unit coating surface area for a given volume of stripping solution over a time period until the solution is considered inactive.

Experiments were conducted using numerous aqueous compositions all containing various proportions of hydrogen peroxide, an acid and an alkali source of hydroxyl ions. The following tables I, II, III and IV identify the different solution compositions all of which had no deleterious effect on the base metal. All of the tests shown in the Tables I, II, III and IV were carried out by immersing a TiN coated Inconel 718* coupon (1.5 x 25 x 50 mm) into the test stripping solution at between 60 and 85° C.

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Table I.

Effect of Citric Acid Content ($\text{H}_3\text{C}_6\text{H}_5\text{O}_7$) on Stripping Efficiency

Solution	Composition Mole/L				pH	Stripping Efficiency (10^{-2} g/cm ² /L)
	H ₂ O	H ₂ O ₂	NH ₄ OH	H ₃ C ₆ H ₅ O ₇		
1	bal.	1.32	1.09	0	10	0.38
2	bal.	1.32	1.09	0.05	10	3.1
3	bal.	1.32	1.09	0.10	10	3.4
4	bal.	1.32	1.09	0.16	10	3.8
5	bal.	1.32	1.09	0.21	10	4.0
6	bal.	1.32	1.09	0.26	10	4.1
7	bal.	1.32	1.09	0.42	9	5.7
8	bal.	1.32	1.09	0.59	9	4.4
9	bal.	1.32	1.09	0.73	8.5	2.0

* Inconel 718 is a registered trademark of the International Nickel Corporation.

Table I should be read in conjunction with Figure 1, which is based on the data of Table I, showing the effect of citric acid on the stripping efficiency of the solution. Citric acid is the preferred acid component although any of the other acids, as heretofore described, may be substituted for citric acid at equivalent concentration or equivalent pH levels to produce substantially equivalent results. The stripping efficiency increases monotonically with increasing concentration of citric acid provided the pH level is above 8.5.

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The concentration of hydrogen peroxide and the alkali component were held constant. It was determined from experimentation that the presence of a minimum concentration of acid was necessary to stabilize the solution and to permit the stripping efficiency to exceed the minimum level. The concentration of citric acid should be above at least about 0.026 mole/L and preferably above 0.052 mole/L. The maximum concentration of citric acid is approximately 0.76 mole/L. Upon exceeding the maximum concentration the pH of the solution drops to below 8.5 which reduces the stripping efficiency below the effective minimum level.

Table II

Effect of NH_4OH Content on Stripping Efficiency

Solution	Composition Mole/L				pH	Stripping Efficiency (10^{-2} g/cm ² /L)
	H ₂ O	H ₂ O ₂	NH ₄ OH	H ₃ C ₆ H ₅ O ₇		
10	bal.	1.32	0	0.16	2	0.39
11	bal.	1.32	0.37	0.16	10	3.0
4	bal.	1.32	1.09	0.16	10	3.8
12	bal.	1.32	1.46	0.16	10	4.2
13	bal.	1.32	1.80	0.16	10	4.0
14	bal.	1.32	2.51	0.16	11	5.3
15	bal.	1.32	3.23	0.16	11	5.1

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Table II should be read in conjunction with Figure 2 which is based on the data of Table II and shows the effect of varying the concentration of ammonium hydroxide (NH_4OH) in the stripping solution. Ammonium hydroxide is the preferred alkali source. The concentration level of citric acid and peroxide were held constant while adjusting the concentration of NH_4OH . From Table II and Figure 2 it is apparent that the stripping solution does not function effectively until the concentration of NH_4OH is raised to a minimum level of about 0.29 mole/L at a pH of 8 or higher. The latter was confirmed by the data shown in Table IV as will be discussed in greater detail later in the specification.

Table III

Effect of H_2O_2 Content on Stripping Efficiency

Solution	Composition Mole/L				pH	Stripping Efficiency (10^{-2} g/cm ² /L)
	H_2O	H_2O_2	NH_4OH	$\text{H}_3\text{C}_6\text{H}_5\text{O}_7$		
16	bal.	0.44	1.09	0.16	9	1.9
17	bal.	0.88	1.09	0.16	9	3.6
4	bal.	1.32	1.09	0.16	10	3.8
18	bal.	2.65	1.09	0.16	10	6.3
19	bal.	4.41	1.09	0.16	10	6.9
20	bal.	2.65	2.17	0.16	11	6.2

Table III should be read in conjunction with Figure 3 from which it is apparent that the stripping efficiency directly increases with increasing

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concentrations of hydrogen peroxide up to about 2.94 mole/L at which concentration the stripping efficiency of the solution levels off. Accordingly, although the hydrogen peroxide concentration may be further increased the maximum level should be about 4.71 mole/L above which, for practical considerations, there is a negative incentive to further raise the hydrogen peroxide concentration. The minimum concentration of hydrogen peroxide is about 0.29 mole/L and preferably above 0.59 mole/L.

Typically the temperature of the solution has an influence on the stripping rate and efficiency. The reactivity of the solution increases with increasing operating temperature and the solution life decreases with increasing operation temperature. Accordingly, to determine the optimum solution temperature two test solutions were prepared using a different peroxide to alkali molar ratio at a constant acid concentration. The stripping rate was evaluated as a function of the operating temperature as shown in Figure 4. The composition of the two test solutions were as follows:

Solution 12. 1.32 mole/L H_2O_2 + 1.46 mole/L NH_4OH + 0.16 mole/L $\text{H}_3\text{C}_6\text{H}_5\text{O}_7$ balance water (marked "O" in Figure 4).

Solution 4. 1.32 mole/L H_2O_2 + 1.09 mole/L NH_4OH + 0.16 mole/L $\text{H}_3\text{C}_6\text{H}_5\text{O}_7$ balance water (marked " Δ " in Figure 4).

The stripping rate is expressed in terms of the total weight loss (in grams) of the coating per unit area (in cm^2) per unit volume (in liters) per

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INTERNATIONAL PRELIMINARY
EXAMINATION REPORT
ANNEX

International Application No. PCT/CH99/00234



Point I

Basis of the report

The present Claim 1 goes beyond the original disclosure content of the application since now an "intermediate carrier layer" without any restriction is being claimed. The original application assumes exclusively a TiN intermediate carrier layer. The basis on page 2, third paragraph of the specification, drawn on by the applicant for the change is only to be read in connection with the preceding paragraph, in which the TiN intermediate carrier layer is disclosed as an essential characteristic. The changes of claim 1, in agreement with rule 70.2 c) PCT, are therefore not taken into account. Consequently, the original claim 1 forms the basis of this examination report.

Point V

Reasoned statement according to Article 35(2) with respect to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Reference is made to the following documents:
D1: DE-A-43 39 502, cited in the application
D2: WO-A-92/07110
2. In his letter dated 27 March 2000 the applicant presents the argument that in D1 a universal removal of all layers is the objective, while the claimed method differs from D1 thereby that it selectively dissolves the intermediate layer, which leads to a large-area detachment of the superjacent hard material layer and, consequently, to an accelerated layer removal. In addition, in D1 it does not appear to be significant whether or not the layers had been applied by PVD or CVD.
- 2.1 The above arguments by the applicant, however, are not reflected in the claims. Claim 1 only describes the task and does not contain any essential characteristics which differentiate the claimed method against the disclosures

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in D1.

3. D1 discloses a method for the selective wet-chemical layer removal of hard material-coated substrates, without their original surface being affected disadvantageously. Subject matter of the invention in D1 is the universal layer removal of all commercially available, ceramic hard material layers of type MeX (Me = Ti, Cr; C = N, AlN, CN) or CrN on cutting, machining and shaping tool surfaces of hard metal. The method in D1 is carried out under the effect of alkaline hydrogen peroxide solutions, which *inter alia* are stabilized with the complexing agents potassium sodium tartrate tetrahydrate ("KNaT") and/or sodium oxalate (*cf.* D2, column 2, line 5 - column 3, line 24). According to Example 2 two TiN/TiAlN duplex-coated indexable inserts had their layer removed within one hour in an alkaline solution containing sodium oxalate, KNaT and H₂O₂, and were subsequently coated again. Since it is not evident in the claims of the present application whether and if other method steps are carried out in order to dissolve the TiN layer through the pores of the superjacent layer (*cf.* clarification objections below, Section VIII), it must be assumed that the method in D1 is the same and that, consequently, the TiN layer perforce goes into solution before the TiAlN layer does. For the consideration of novelty it is immaterial whether or not in D1 a selective layer removal of the intermediate layer was considered.
- 3.1 The disclosures in D1 are prejudicial as to novelty with respect to claims 1 to 3, 5 to 8 and 10 to 12.
4. Claims 4 and 9 relate to conventional layer thicknesses for intermediate layers comprising TiN and for hard material cover layers. Claim 13 claims the exclusive presence of H₂O₂, KNaT and/or disodium oxalate and NaOH. In neither measure can any inventive contribution be discerned. The effectiveness of such compositions for removing TiN layers is known (*cf.* D2, pages 4 and 5). D1, moreover, discloses that the remaining solution can be supplied to a conventional waste water treatment facility (*cf.* column 3, lines 51 to 53), consequently it is also not possible to detect any advantages with respect to ease of disposal.

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5. Therefore claims 1 to 13 do not satisfy the requirements of Art. 33 PCT.

Point VIII

Certain Observations on the International Application

1. Claim 1 does not contain all of the essential characteristics. The complete layer removal of TiN and other hard materials (TiAlCN, TiCN, CrN) for example with basic hydrogen peroxide solutions comprising KNaT (*cf.* claims 9 to 12 of the application) is known per se (*cf.* D1). According to D1 this method for layer removal is not selective for TiN but rather the solution also attacks the other hard materials. However, the application does not reveal which other measures are required for a selective removal. The resultant formulation "that the hard material layer is removed by selectively dissolving the TiN layer through the pores of the hard material layer" does not provide a person skilled in the art with the means required for the "selective dissolving".
2. Claim 1 therefore does not satisfy the requirements of Art. 6 PCT.

